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Chemistry and Physics of Glass

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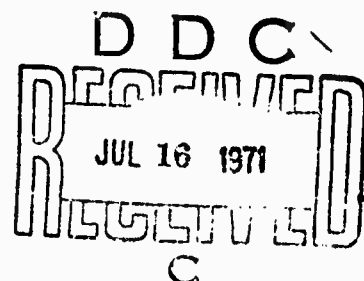Contractor: Naval Research Laboratory

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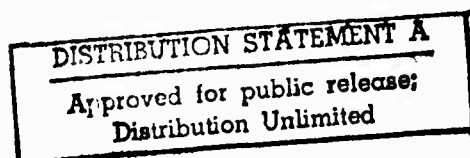
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I. Introduction

This report describes work done under the sponsorship of ARPA Order No. 418 during the first half of 1971. Previously the principal areas of investigation under this contract have included the preparation of ultrahigh purity glasses, the optical and electrical properties of glasses and the nature of radiation-induced defects in simple glasses. Much of this work has now reached the publication stage and some of the highlights are discussed here. These include the development of a platinum free laser glass, the discovery of several new radiation centers in borate glasses, evidence of local order in liquid chalcogenides, and the invention of a chalcogenide glass bolometer for broadband detection of infrared and microwave radiation. During this period there has been increased emphasis on the structural studies of glasses by means of x-ray and neutron diffraction and the initiation of a new program focussed on the mechanical properties of glasses. A new biaxial tensile testing facility was put into operation and programs are underway to develop high strength glasses by techniques such as ion implantation, valence variation and surface coatings. Details of progress in these and other areas are described in the following sections of this report.

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II. Progress

A. Strength of Glass

Initial efforts were directed toward the selection of a suitable test method for the strength of glass the the construction of the appropriate apparatus. Emphasis was placed on finding a method which could yield reliable statistical data on a small number of test samples. The new biaxial flexure method recently developed by NBS for ceramic substrates was chosen as the primary method of (tensile) strength measurements. This method supports a disk (approximately 1.25" dia.) on three balls and loads the disk in the center with a vertical rod. Like the ball-on-ring and ring-on-ring plate tests, this method eliminates edge effects. However, the three-ball support test has three advantages: (1) there is an exact solution for the stress; (2) it does not require near as demanding flatness tolerances, and (3) it has been developed with smaller specimens that are more amenable to laboratory study. Further, in a NBS sponsored round-robin series of tests, this method showed coefficient of variation as follows: 12.4% for single tests; 6.9% for five tests; and 5.8% for ten tests, for various commercial Al_2O_3 substrates among eight laboratories.

During this reporting period, a ball and piston test apparatus has been designed at NRL. The vertical rod has been coupled to an Instron machine. Results on ground and polished fused silica (GE 125, Corning 7940) disks appear quite promising with a coefficient of variation of 15% in a 20 sample test. Since the object of this program is to develop glasses which possess significantly higher strength than those presently available, this test method appears to be more than adequate for our investigations. Plans

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call for testing of fused silica, soda lime, borosilicate, lead silicate and alkali aluminosilicate glasses by this method under a variety of environmental conditions. Work is currently underway to determine the effects of traces of water in fused silica on its mechanical properties and its surface properties. The small size of the samples will allow us to test glass discs prepared and treated in our own laboratory. This includes those treated by ion implantation, valence variation and ion exchange.

1. Ion Implantation

The most successful techniques of strengthening glass at present are those which introduce a compressive stress at the surface such as thermal tempering, diffusive exchange of surface alkali ions, and surface crystallization. With this in mind, a program has been initiated to study the effects of ion implantation on the mechanical properties of glasses. A 5 MeV Van de Graaff has been used to accelerate neon, phosphorus and boron into fused silica samples. Surface concentrations of 10^{16} ions/cc have been achieved. The samples show only slight evidence of radiation damage as detected by optical and ESR measurements. Because of experimental limitations at the accelerator, the implanted samples have been small, typically 1 cm square. However, a beam deflector is being installed on the NRL Van de Graaff which will permit ion implantation over the entire area of the 1.25" diameter disks used in the tensile test apparatus.

The advantages of the ion implantation technique include the high concentration of ions which can be stuffed into the surface (which hopefully means a high surface stress) and the wide latitude of species which can be accelerated. The disadvantages are the

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shallow depth of penetration and the unknown effect of surface
radiation damage on the strength of the samples. Some of
these questions should be resolved in the next few months.

2. Valence Variation

Preliminary experiments on the strengthening of glass
by valence variation have included work with manganese,
chromium, and vanadium-containing glasses. The intention is
to produce surface compressive stresses in glasses either by
reducing or oxidizing a multivalent ion at a glass surface. If
reduction can be produced at a temperature below the strain
point without loss of oxygen from the composition, or if oxidation
can take place with an increase of combined oxygen, surface com-
pressive strains should be produced. The former method is
illustrated for the case of manganese-containing glass in a patent
specification (Fischer, U.S. 3,460,927). The latter process is
disclosed, but not illustrated in detail, in another patent (Loukes
et. al. U.S. 3,453,095).

Attempts to duplicate the reported results with the manganese
glass were unsuccessful. Rather than purple glass containing
Mn^{3+} as reported, our synthesis produced brown glass containing
Mn^{2+} in agreement with our previous experience in the synthesis
of similar manganese doped glasses. Attempts were made to
oxidize the surface of the brown glasses, but the purple color of
the Mn^{3+} ion was observed only when the reduction procedure was
conducted at temperatures which produced devitrification of the
glass.

Both the oxidation and reduction procedures were attempted
on chromium doped glasses without producing evidence of valence

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change. Glass containing 3% Cr was prepared in an oxidizing atmosphere and was found to contain both Cr^{3+} and Cr^{6+} ions by optical absorption measurements. No evidence of any surface reduction of Cr^{6+} ions was obtained by heating in hydrogen at temperatures lower than those that produced devitrification. A similar glass when prepared in a reducing atmosphere contained the chromium as Cr^{2+} and Cr^{3+} ions. Attempts to oxidize the Cr^{2+} by heating in oxygen below the devitrification temperature were not successful.

A more promising result was obtained with a vanadium-bearing glass. A soda-lime glass containing 1.2% V melted in an air atmosphere has a light yellow-brown color and luminesces when excited by 365 or 254 nm ultraviolet. After treatment of this glass with hydrogen at $450^{\circ}C$, the luminescence response under 254 nm excitation was observed to have been quenched. The quenching may be due to reduction of the V^{5+} ion at the surface. Since the glass is highly absorbent at 254 nm the luminescence observed at this wavelength originates at the surface. Reduction is believed to produce a vanadium species which is highly absorbent at this wavelength but which does not luminesce. The above conclusions are the results of only visual observations. Larger samples are to be prepared to permit optical measurements and to determine whether strengthening is achieved by valence change.

3. Compressive Strength of Glass

Another area of investigation has been the compressive strength of glass. Cylindrical specimens with a reduced gauge section, along with end shims, (to minimize end effects and associated tensile stresses) are being prepared. There are two

separate interests in compression testing. First, in Ernsberger's elegant testing using pristine bubble surfaces, his limited room temperature compressive data agreed with his more extensive ultimate tensile strengths. Because of (1) the high stress levels (0.5 - 1.2 x 10^6 psi), (2) the consistency of the results, and (3) the temperature variation, these tests suggest an intrinsic failure stress level. Further tests, especially in compression, are required to explore this further. The second basic interest in compression testing stems from Outwater and Gerry's report of a definite self-luminescence around the origin of fracture in compression (adequate to allow photographing the fracture by its own luminescence). Since this phenomena was only observed with high stress failures (where no parasitic stresses appeared to be present) and was accompanied by a change in fracture mode, this again suggests a possible intrinsic compressive failure mechanism. Further, useful information may be contained in the luminescence. The Optical Materials Branch at NRL has the capability of spectrally resolving luminescence pulses to determine whether they might contain useful data.

4. Effects of Surface Finishing on Strength

Studies of the effects of surface finishing on strength have continued. In a NRL study of crystalline ceramic materials it has been found that the strength can depend substantially on the direction of grinding. Specimens tested as ground where the grinding direction was perpendicular to the tensile axis, can have the same or substantially lower (up to 50% less) strength than specimens ground parallel to the tensile area. A major factor in this difference in strength depending on grinding direction is the hardness - the

difference in strength increases with increasing hardness. Initial
tests on glasses indicate the same trend with hardness.   Further
investigation of this is planned since it may contain both basic and
practical information. Basic information may be obtained since
this effect appears to be related to both deformation and fracture
processes in the surfaces of crystalline ceramics, and hence
may provide such information on glasses. Such directional effects
are also of practical interest since some glass pieces are tested
or used with ground surfaces and such results are pertinent to
them. Thus, for example in studying abraded (e. g. ground) glass
samples, such direction effects must be known to properly compare
uniaxial and biaxial testing results.

B.   Protective Coatings on Glass

It is generally accepted that water plays an important role
in the stress-induced corrosion of vitreous materials. Organic
coatings, based principally on alkyl silane derivatives, have been
developed as a means of rendering the glass surface hydrophobic.
Although generally effective, such water-repellant films are often
degraded by slow hydrolysis and abrasion. Reagents other than
the alkyl silanes have not been investigated in this context, and a
general synthetic scheme for formulating hydrophobic surface
films would be extermely useful.

Previous investigations of the chemisorption of, for example,
BCl_3 on the silica surface have led to the conclusion that adjacent,
interacting pairs of surface silanol ($\equiv Si\text{-}OH$) groups react to form
a bridging species, $(\equiv Si\text{-}O)_2 BCl$, and isolated silanols form a non-
bridging entity, $\equiv Si\text{-}OBCl_2$.   It has been further concluded that the

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non-bridging species hydrolyze to form $B(OH)_3$ and the original $\equiv Si-OH$ but that the bridging structure forms a stable hydrolysis product, $(-Si-O)_2BOH$. This suggests that the possibility of using the bridging $(\equiv Si-O)_2BCl$ as an intermediate in the synthesis of a new variety of organic coating in which the alkyl group replaces Cl on the bridging site. One way this might be done is to photochemically react an alkyl halide with the chemisorbed inorganic halide.

With this goal in mind, the chemisorption of BCl_3 on silica has been re-investigated using infrared spectroscopy. By using thin layers of the powdered substrate and compensating for absorption by the SiO_2, it was possible to obtain spectra of the various surface species down to 250 cm^{-1}, even in the region of strong substrate absorption. The results of this study, in conjunction with earlier work, indicate that geminal free hydroxyl groups, $\equiv Si(OH)_2$, must be considered as a third distinct type of surface species, capable of forming a second bridging structure, $\equiv Si(-O-)_2BCl$, and a corresponding hydrolysis product. It has, until now, been assumed that geminal sites react in the same manner as isolated silanols, forming non-bridging species, and it is somewhat encouraging to note that the final concentration of nonhydrolyzable bridging structures is higher than had been anticipated.

The next experiment in this series will be an attempt to replace Cl in the bridging chemisorbed species with methyl groups. Highly reactive methyl radicals, CH_3, will be generated by the gas-phase UV photolysis of methyl iodide (CH_3I), and infrared spectroscopy will be used to examine the resulting surface species

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for evidence of B-CH_3 groups. Water vapor adsorption iso-
therms can then be obtained as a quantitative measure of the
reduction in hydrophilicity of the surface.

C. Theory of Fracture in Disordered Systems

Most theoretical treatments of fracture phenomena in
glasses are based on a consideration of the surface energy of the
developing crack and the concentration of stresses at the crack tip.
A complementary approach on a microscopic level, in which the
statistical mechanics of the glass network is considered, has not
yet been attempted.

If the vibrational density-of-states function (frequency spec-
trum) of the system can be calculated before and after the forma-
tion of a crack, the change in free energy (ΔF) for the process
can be derived. A knowledge of ΔF/per unit crack length for a
variety of different crack paths may lead to an understanding of
the effect of local density fluctuations on the fracture process.
The temperature dependence of the strength of glass (the breaking
tensile stress of fibers, for example) is not generally well under-
stood, except at low temperatures, where a single activation
process appears to dominate. A full treatment of the thermo-
dynamics of the fracture process is expected to yield information
on the high-temperature strength characteristics. Finally, it
would be very useful to know whether the so-called "Griffith flaws"
are present only as a result of abrasion and corrosion or are,
perhaps, formed intrinsically to minimize the free energy of the
system, in much the same manner as a certain number of defects
are formed in a real crystal.

Since the calculation of frequency spectra of disordered systems is quite complicated, a simple glass-like disordered system - a diatomic chain in two dimensions - has been chosen as a starting point for the development of the necessary computer programs. The system, also generated by computer, incorporates the essential features of vitreous disorder - randomized relative orientation of adjacent structural units and randomized bond angles between units, and the frequency spectrum of the corresponding ordered system can be obtained in closed form for comparison with that of the disordered chain. One intriguing result of this study is the great difference in the degree to which the disorder affects the acoustic and optic modes. A similar phenomenon has been noted in the results of cold-neutron scattering experiments with vitreous and crystalline quartz.

At present, this approach is being extended to a more realistic system - the $A_2 B_3$ disordered network in two dimensions. Since this is a true network, not merely a chain, it will be possible to perform some of the thermodynamic calculations outlined above. The program for calculation of the frequency spectrum is already in operation, and the program for generation of the network is in the final stages of development.

D. <u>Other Theory</u>

The theoretical investigation of x-ray emission and absorption in SiO_2 has continued in two directions. First, calculations of energies and transition probabilities within the framework of the valence bond picture have been made for the Si Kβ and $L_{2,3}$ as well as the O K$_\alpha$ emission spectra. The agreement with

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experiment has been found to be excellent in the latter, but
only qualitatively accurate results have been obtained in the
former. Second, investigations have been made into the possi-
bility that localized defect centers are produced in the radiative
processes.

This point is particularly important since in the valence bond
picture, either x-ray luminescence or the emission of high energy
Auger electrons results in bond breaking and the creation of para-
magnetic centers - a result not usually predicted by the usual bond
pictures. In line with this, the transient centers which have been
produced with pulsed high energy electrons may have involved
the same processes. Several models for such transient defect
centers are under investigation together with the permanent center
investigated long ago by Obrien which is corrected with the
presence of Al as an impurity. Since Al has one less electron
than Si, the resulting localized hole may have similar properties
to the transient radiation produced defects under investigation.

E. The Structure of Silica Glass

The structure of silica glass has been investigated exten-
sively owing to the fact that it is considered a basic representative
of the glassy state. During the past year at NRL both x-ray and
neutron diffraction data have been collected with a high degree of
statistical accuracy to large scattering angles ($\underline{s} \sim 18$ for x-rays
and $\underline{s} \sim 23$ for neutrons, where $\underline{s} = \frac{4\pi \sin \theta}{\lambda}$, 2θ is the angle
between the incident and diffracted beam and λ is the wavelength).
New methods of analysis have been developed that allow the calcu-
lation of very accurate radial distribution functions. These methods
constrain the radial distributions to be consistent with known physi-

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cal and mathematical properties of the system. Through these techniques, it has been demonstrated that much more structural information than previously recognized is present in the diffraction data. The radial distributions contain significant details out to ~ 13 A in contrast with the earlier studies that indicated no details beyond 7 A. This signifies that a considerably greater degree of ordering in the silica glass structure is present than has heretofore been supposed. The ordered phase has been tentatively identified and studies are proceeding to establish definitely the character of the ordering and its amount. These include comparisons with known crystal systems in order to determine the nature of the ordering with a minimum of ambiguity. Computer programs for model construction to confirm the characterization of the ordering and the structure of the glass are being prepared.

Experiments are being conducted to determine the stability and reproducibility of the ordered structure in silica glass. Melts have been made of quartz crystal. In addition, silica glass has been heated for various periods of time extending from about ten minutes to several days at temperatures above and below the softening point. In every case, the x-ray diffraction analysis of the bulk structure has shown the same structural pattern. Care was taken in each of the experiments to remove outer surface structures which form rapidly under conditions of high temperature for long periods. At this point, minor variations among the radial distribution curves appear to fall within experimental error. It appears that very precise analyses will be required to determine changes, if any, in the ordering.

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Investigations have begun on the structure of As_2Se_3 glass. In this problem, it will be of considerable advantage to employ neutron diffraction rather than x-ray diffraction data. The high absorpt`n of the heavy atoms for x-rays interferes seriously with the collection of accurate data and the relationship to bulk structure is uncertain. In contrast, no such difficulty accrues from the neutron diffraction experiment. Preliminary data indicate a higher degree of ordering than that found in silica glass, in agreement with indication from solid state spectroscopy. The neutron diffraction experiment will be pursued with improved counting statistics.

F.   Platinum Contamination in Glass

Glasses melted under oxidizing conditions in platinum crucibles contain both dissolved Pt^{4+} ions and metallic particles. In glasses melted without stirring, some of the metallic particles are found to be embedded in the glass although most seem to remain on the surface. In glasses melted under nonoxidizing conditions, platinum contamination is significantly reduced with only some surface particle contamination being present, the amount depending on glass composition and melting temperature. The above conclusion is the result of NRL investigations of glasses of varying composition and of analyses which were made on both surface and bulk portions of the glasses.

In previous work the determination of surface platinum depended upon microscopic examination and the use of a colorimetric method of chemical analysis sensitive to 1.0 µg of Pt. Three additional techniques have now been employed for this determination. They are: (1) emission spectrographic analysis which is sensitive to

0.1 µg, (2) mass spectrographic analysis, sensitive to 0.02 µg, and (3) neutron activation analysis sensitive to 0.02 (0.2 µg in glasses containing calcium). For the determination of platinum bulk glass the mass spectrograph (sensitivity of 50 parts per billion) and neutron activation analysis (sensitivity of 3 - 30 ppb depending on presence of Ca) have been used. The activation analyses were conducted at the National Bureau of Standards; the other chemical analyses were performed in our laboratories.

Tables I and II compare the composition and platinum contamination of the new NRL laser glass with those of two standard laser matrix compositions melted under reducing conditions. Surface platinum is reported in micrograms collected from sample surfaces of about 10 cm^2. Volume or bulk platinum is in parts per million by weight. Platinum was not detected in bulk portions of any of these glasses. The neutron activation technique could not be applied to the alumino-silicate glass because of its high lithium content, and its sensitivity for the analysis of the NRL glass is restricted by the presence of calcium. Surface platinum was detected microscopically on the aluminosilicate and barium crown glasses, but not on the NRL glass. Only the mass spectrograph was able to detect platinum on this latter material. The reported figure of 0.02 µg Pt in the NRL glass represents an improvement of a factor of 50 - 500 over earlier laser glass compositions. In the present work the melts were not stirred, and the platinum deposits remained on the glass surface. In a production process they would be stirred into the melt to produce damaging inclusions.

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TABLE I

Compositions of Laser Glass Matrices (Mole Percent)

Glass	Li_2O	Na_2O	K_2O	MgO	CaO	CaF_2	BaO	Al_2O_3	SiO_2
Aluminosilicate	27.3				11.4			2.7	58.6
Barium Crown	2.5	7.5	7.6				2.5	1.3	78.6
NRL Glass	3.4	10.3		1.2		2.3		3.2	79.6

TABLE II

Platinum Contamination of Glasses

Glass	Surface	Bulk	
Aluminosilicate	10.5 (1)	< .05 (3)	
Barium Crown	1 - 4.9 (2)	< .05 (3)	< .003 (4)
NRL Glass	0.02 (3)	< .05 (3)	< .03 (4)

(1) Colorimetric analysis

(2) Colorimetric and neutron activation analyses

(3) Mass spectrographic analysis

(4) Neutron activation analysis

Preparation of samples doped with Ce_2O_3 and Nd_2O_3 indicated that the introduction of laser dopant ions presented no special problems. These preparations were equally free of platinum. In an experiment more consistent with commercial glass melting practice, a sample was prepared in which the silica was provided as sand, and the raw materials were simply dry blended and then melted in an argon atmosphere in a platinum crucible. No evidence for platinum contamination of either the surface or bulk of this sample was found with any analytical technique.

The valence state of some impurity ions is affected by melting in a nonoxidizing atmosphere. Copper and iron are present mainly as Cu^+ and Fe^{2+} in glass melted in 90% CO-10% CO_2, and some elements such as lead may be reduced to metals. The absorption due to the lower valence state may be especially deleterious, such as the Fe^{2+} absorption at the neodymium laser wavelength, and reduced metallic impurity particles may serve to produce damage as does platinum. Accordingly, it would be of interest to investigate the behavior of more of the common impurity ions in the nonoxidizing atmosphere, to develop raw material sources which are satisfactorily free of such impurities, or to develop glass melting procedures which yield such impurity traces in a dissolved innocuous form without suffering platinum contamination.

G. Radiation Damage in Alkali Borate Glasses

During the recent contract period, studies of radiation damage in alkali borate glasses were concentrated on electron-spin-resonance properties of three defect centers: (1) the boron electron

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center (BEC), (2) the alkali electron center (AEC), and (3) the halogen-atom hole center (HAHC), all of which are produced by x irradiation at cryogenic temperatures.

1. The Boron Electron Center

A number of possible descriptions for the BEC were considered in a recent paper, including the model involving an electron trapped in a boron-oxygen antibonding orbital, and the model of an electron trapped in a dangling boron hybrid orbital. Of these, the latter has emerged at the most plausible. Dangling boron orbitals at the sites of oxygen vacancies or 3- and 4-coordinated borons would be quite similar to the orbitals of the unpaired spin on the unknown radicals BO_2^{2-} and BO_3^{4-}, respectively. That the BEC could be comparable to either of these structures is demonstrated by comparing the boron 2s-state density as determined by ESR with the apex-atom 2s-state densities for the isoelectronic species (CO_2^- and NO_2) and CO_3^{3-} and NO_2^{2-}), respectively.

Two facts suggest that alkali ions may be involved in some way with the formation of the BEC. First, the BEC has not been observed in "pure" B_2O_3 glass, and, second, the boron hyperfine coupling constant is found to increase by approximately 5% as potassium is replaced by sodium or sodium is replaced by lithium. However, no conclusive evidence of a hyperfine interaction with alkalis is apparent in the BEC spectrum. Based on line-width measurements it is estimated that the maximum delocalization of the BEC wavefunction into an alkali ns state is about 10%.

Two possible roles for the alkali ion are suggested. The first role places the nearest alkali ion some distance away from the defect and off of the axis of the dangling orbital. In this picture, the variation in the BEC boron hyperfine coupling constant is seen to result from a general stretching of the boron-oxygen

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network as larger alkali ions replace smaller ones. While
this model would explain the low upper limit on possible hyper-
fine interactions with alkalis, it does not account for the fact that
the presence of alkali ions in the glass is evidently required for
BEC formation. In the second possible role, a three-electron,
covalent bond is envisioned as forming between the defect boron
orbital and an alkali ion. In such a case the character of the
bonding orbital (containing paired spins) would be predominantly
that of the appropriate alkali core state and would increase in the
sequence K $\rightarrow$ Na $\rightarrow$ Li. Conversely, the character of the anti-
bonding orbital (containing the unpaired spin) would be predominantly
that of the boron sp hybrid and would also increase in the same
sequence,as observed experimentally. This latter model, while
still lacking direct experimental or theoretical foundation, would
clearly explain the failure to obtain the BEC in boron-oxide glass
containing no alkalis.

The boron hyperfine coupling constant for the BEC shows nearly
step-wise variations with changes in glass composition. These
variations do not correlate well with either the so-called "boric-
oxide-anomaly" or the number of four-coordinated borons as
determined by nuclear magnetic resonance. They do, however,
correspond to postulated variations in types and numbers of boron-
oxygen ring structures thought to exist in these glasses. The BEC
is now believed to be a dangling boron orbital at the site of an
oxygen vacancy on the perifery of an otherwise intact ring structure.
(It is possible that an alkali ion may be attached at this site.)
Thus, the BEC may turn out to be a useful "probe" of structure of the
order of 5 $\overset{o}{A}$ in alkali borate glasses.

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2. Alkali-Associated Electron Centers

The maximum concentrations of BEC defects in alkali borate glasses have been measured to be $\sim 15\%$ of the total population of trapped holes. Research carried out under this contract has now demonstrated the probable fate of the remaining $\sim 85\%$ of the trapped electrons. As mentioned in the previous Semiannual Report, a new type of defect has been recognized; this was termed the alkali electron center or AEC. On the basis of recent computer simulations of the ESR spectra, it.has been concluded that the AEC comprises a class of defects ranging from alkali atoms to complexes of many alkali ions which have trapped one or more electrons.

The computed spectra tend to support the existence of K^0 and/or K_2^+ in potassium borate glasses containing $\leq 20\%$ K_2O. Whichever interpretation is correct, these centers appear to be correlated with the prominent radiation-induced optical band at 1.5 eV. In glasses containing 30% K_2O or 30% Na_2O, the best simulations corresponded to paramagnetic complexes of 4 potassium or 6 sodium ions, respectively. No separate resonance due to lithium-associated centers is observed in lithium borate glasses of the same composition, nor is the blue coloration anywhere near as intense. One possible explanation is that no lithium-associated centers are formed, but this would leave open the question of where the electrons are trapped in the lithium borate glasses. A better explanation, though still conjectural, is that much larger complexes of lithium are formed (10 or more lithium ions), resulting in far narrower ESR spectra which would become buried under central boron-oxygen-hole-center spectrum. If this is the correct picture, then it is possible to explain the disappearance of the

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potassium- and sodium-associated centers when the samples are thermally annealed at room temperature by assuming that only electrons trapped on the larger complexes of alkali ions are stable at the higher temperature. Experiments to check this hypothesis are being planned.

3. Halogen-Atom Hole Centers

Studies of radiation-induced defects in halide-doped alkali borate glasses have been described in the past several Semiannual Reports with emphasis on the measurements which bear on the kinetics of defect formation and decay. One of the most important defects was the halogen atom, formed by competitive hole trapping at halide ions. During the last six months a concerted effort has been made to derive the sets of spin Hamiltonian parameters which characterize the Cl^0 and Br^0 defects. The ESR spectra of both of these species have finally been computer simulated with fairly high fidelity, leading to several remarkable discoveries. First, it was found that the hyperfine tensors of both centers were axially symmetric with $|A_\perp| \approx 1/2 |A_\parallel|$. This tends to verify that the ground state of each center is a $p_x^2 p_y^2 p_z^1$ configuration, as expected for such atomic species. Moreover, values of $\langle r^{-3} \rangle_{np}$ as calculated from the measured hyperfine splittings compare closely with published theoretical values, providing perhaps the first experimental measurement of this parameter. Second, the symmetry of the g tensor was found to be approximately axial in each instance. Further, it has become evident that $g_\perp$ is the only spin-Hamiltonian parameter to be significantly affected by random influences in the glass. According to theory already in the literature for the principal g factors of a $p_x^2 p_y^2 p_z^1$ configuration, the following relation

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should be approximately satisfied: $g_\perp = g_\parallel (1 + \ell\lambda/E)$, where λ is the spin-orbit coupling constant, $E = E(p_z) - E(p_x, p_y)$ and ℓ is a factor of the order unity. The most remarkable finding has been that the ESR spectra of both Cl^O and Br^O can be accurately simulated under the assumption of $\ell \sim 0.7$ and a Gaussian distribution of energy splittings with $E_{ave} \sim 1.6$ eV (Halfwidth ~ 0.8 eV0, using published values of λ. To explain the close parallel which exists between the g tensors of these two species, the possibility is being considered that each halogen atom in this glassy matrix is intimately associated with an alkali ion. Thus, the present species may be the molecular ions $(KCl)^+$ and $(KBr)^+$. Such a situation would be analogous with the model for the BEC which postulates a covalent bond with an alkali ion.

H. Semiconducting Glasses

The far infrared studies of vibrational modes in vitreous As_2Se_3 and $Tl_2SeAs_2Te_3$ have been extended to high temperatures. Room temperature studies demonstrated that the vibrational absorption peaks between 50 and 100 microns in these glasses have Gaussian lineshapes, in contrast to the Lorentzian lineshapes observed in crystalline materials, and that the Gaussian linewidth provides a new fundamental parameter to characterize the structural disorder. The high temperature infrared absorption spectra of these glasses reveal that the vibrational absorption bands (and their Gaussian lineshapes) persist in the liquid phase and are an indication of the preservation of local order in the molten glass. In $Tl_2SeAs_2Te_3$ glass there is a well-defined temperature $T_2 = 480^O K (> Tg)$ above which the vibrational modes disappear. Similar behavior

is predicted for all layer-type semiconducting glasses, and T_2 is proposed as a characteristic temperature for an abrupt change of local order in these materials.

The highly conducting $Tl_2SeAs_2Te_3$ glass exhibits a frequency independent thermally activated absorption at wavelengths between 3 and 50 microns with an activation energy approximately equal to that for dc conductivity. This represents the first free carrier or electronic optical effect to be observed in a semiconducting glass. Its frequency independence is consistent with a microscopic mobility at infrared frequencies of less than 3 cm^2/V sec. The study of this effect has now been extended to temperatures far above Tg and the thermally activated absorption is found to be dominant even in the 50 to 100 micron range at temperatures in excess of T_s, where the vibrational absorption bands disappear.

Recently, the structural studies of the $Tl_2SeAs_2Te_3$ glass have been extended to include [205]Tl and [203]Tl nuclear magnetic resonance (NMR). Large chemical shifts of the thallium NMR (0.25%), which are relatively temperature independent, demonstrate that the thallium is strongly covalently bonded to the structural network in both the solid and liquid states of the glass. These results are in agreement with the conclusion of the preservation of local order in the melt which was drawn from the high temperature infrared studies.

The properties of the $Tl_2SeAs_2Te_3$ glass have been utilized in the invention of a room temperature thermistor bolometer for broad band detection of infrared and microwave radiation. These chalcogenide glass bolometers can be fabricated by simple hot-pressing or evaporation techniques, making possible the production

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of large number of low-cost uniform single element bolometers or multi-element bolometer arrays.

III. Publications and Presentations

Vibrations of Glass-Like Disordered Systems I: Diatomic Chains in Two Dimensions, V. M. Bermudez, J. Chem. Phys. $\underline{54}$, 4150 (1971); also reported at New York City A. P. S. Meeting, Feb. 1971, (Bull. A. P. S. $\underline{16}$, 52 (1969)).

Infrared Study of BCl_3 Chemisorbed on Silica Gel, V. M. Bermudez, J. Phys. Chem. (to be published - J. Phys. Chem.).

ESR Studies of an Intrinsic Trapped-Electron Center in X-Irradiated Alkali Borate Glasses, D. L. Griscom, accepted for publication - 1 August 1971, J. Chem. Phys.

Di-Alkali Molecular Ions in Irradiated Alkali Borate Glasses, D. L. Griscom, Bull. Am. Phys. Soc. $\underline{16}$, 447 (1971).

Vacuum Ultraviolet Absorption in Alkali Doped Fused Silica and Silicate Glasses, G. H. Sigel, Jr., accepted for publication - J. Phys. Chem. Solids.

Luminescence Due to Impurity Traces in Silicate Glasses, R. J. Ginther and R. D. Kirk, accepted for publication - J. Non-Cryst. Sol.

Laser Stimulated Thermoluminescence in Glass, R. J. Ginther and E. W. Claffy, accepted for publication - J. Appl. Phys.

The Role of Alkali in the Formation of Radiation Induced Defect Centers in Simple Silicate Glasses, G. H. Sigel, Jr., accepted for publication - Proc. of the Ninth International Congress on Glass, Sept. 1971.

Platinum Contamination of Glass, R. J. Ginther, submitted for publication - J. Non-Cryst. Solids.

The Effect of Grinding Direction on the Strength of Ceramics, to be published - Proc. of the Conference on the Science of Ceramic Machining and Surface Finishing.

Far Infrared and Microwave Conductivity Spectrum of Semiconducting $Tl_2SeAs_2Te_3$ Glass, S. G. Bishop, P. C. Taylor, D. L. Mitchell, and L. H. Slack, J. Non-Cryst. Solids $\underline{5}$, 351 (1971).

One-Phonon Spectra of Amorphous Semiconductors, P.C. Taylor, S.G. Bishop, and D.L. Mitchell, Proceedings of International Conference on Phonons, Université de Rennes, 26-28 July 1971.

Infrared Conductivity in Semiconducting Chalcogenide Glasses, (Invited) D. L. Mitchell, 4th International Conference of Amorphous And Liquid Semiconductors, University of Michigan, 9-13 August 1971.

Temperature Dependence of Local Order in the Layer Type Liquid, Semiconductors As_2Se_3 and $Tl_2SeAs_2Te_3$, P.C. Taylor, S.G. Bishop, and D. L. Mitchell, submitted to Phys. Rev. Letters.

Chalcogenide Glass Bolometers, S.G. Bishop and W.J. Moore, Proc. of the Special Meeting on Unconventioanl Infrared Detectors, Naval Electronsic Laboratory Center, San Diego, Calif., pg. 147, April 1971.

Temperature Dependence of the Vibrational Absorption Peak in Semi-conducting Chalcogenide Glasses, P.C. Taylor, Bull. Am. Phys. Soc., Series II, 16, 303 (1971).

Thermally-Activated, Band-Type Conductivity at Infrared Frequencies in Semiconducting Chalcogenide Glasses, D.L. Mitchell, S.G. Bishop, and P.C. Taylor, Bull. Am. Phys. Soc., Series II, 16, 303 (1971).

Chalcogenide Glass Bolometers, S.G. Bishop and W.J. Moore, Bull. Am. Phys. Soc., Series II, 16, 303 (1971).

Infrared and Microwave Optical Properties of Semiconducting Chalcogenide Glasses, P.C. Taylor, NRL Physics of Solids Colloquium, 13 Jan. 1971.

Contract with Bausch and Lomb

Contract N00014-67-C-0552 with Bausch and Lomb, Inc. expires on 30 June 1971. However, in order to complete ongoing research projects and the subsequent preparation of reports, Bausch and Lomb has requested a time extension without extension of funding. A request that the contract be so extended for a period of six months has been communicated to the contract office of ONR.

In the present period the work has been principally concerned with the development of a melting procedure for large (400 g.) samples of the NRL developed laser glass matrix, and of an optical inspection technique for platinum particles in samples of this material.

Some compositional variation of the NRL developed formula has been studied in order to determine whether the viscosity of the original glass could be reduced. No substantial viscosity reduction was obtained, so subsequent work has been with the original composition. The main problem encountered in the induction melting of the larger samples has been the development of a suitable induction coil and of a coil and crucible geometry which provides a uniform heating system. No uniform heating can lead to melting of the platinum crucible which serves as the susceptor. Very promising results have recently been obtained with a closely coupled coil which has small ceramic separators between turns.

The assembly of an apparatus for the detection of platinum particles in glass is nearly complete. It consists of an arrangement for immersing the glass in a liquid of appropriate refractive index, a laser or focussed light source to illuminate the glass, and a microscope which can scan the illuminated specimen. This equipment will be used to examine the experimental melts in the near future.

Publications by Bausch and Lomb

Optical Absorption and Color Caused by Selected Cations in High Density Lead Silicate Glass, J. L. Stroud. To be published in August 1971 issue of Journal of the American Ceramic Society.

Optical Absorption of Lead in Glass, J. L. Stroud and E. Lell. Submitted for publication in Journal of the American Ceramic Society.